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Field Test of Produced Water Treatment With Polymer Modified Bentonite

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Abstract

The combination of ET Ventures' ET #1 and granular activated carbon consistently and effectively removed hydrocarbons from Tensleep formation produced water in a 24-hour test at Teapot Dome oil field. Specific findings are that ET #1:

- Reduced Total Petroleum Hydrocarbon (EPA Method 418.1) to non-detectable levels.

- Reduced Oil and Grease (EPA Method 413.2) to non-detectable levels.

- Reduced soluble hydrocarbons: Benzene, Ethylbenzene, Toluene, and Xylene (BTEX- EPA method 8020) to barely detectable levels. BTEX was below detectable limits after the combination of ET #1 and granular activated carbon.

Introduction

This report describes the results of a test conducted at the Rocky Mountain Oilfield Testing Center (RMOTC) of a product manufactured and marketed by ET Ventures, L.L.C. This product, ET #1, is designed to adsorb hydrocarbons from wastewater. The test conducted at RMOTC was intended to document the ability of ET #1 to:

- Adsorb a relatively large quantity of hydrocarbons from oilfield produced waters carrying a free oil sheen.

- Tolerate the wide variations in hydrocarbon concentrations typical of oilfield operations.

- Adsorb soluble hydrocarbons in the BTEX family under these same circumstances.

A 24-hour test was designed in which produced water from the Tensleep formation was flowed through a three-stage treatment system composed of two stages containing ET #1 and a final polishing stage containing granular activated carbon (GAC).

Product Description

ET #1 is a product generally referred to as a polymer modified bentonite or an organoclay. This group of materials is manufactured by binding an amine polymer onto bentonite clay and drying it in a granular form. The polymer binds to the bentonite's ionic surfaces and converts the clay from a hydratable form to an oil-wet, hydrocarbon adsorbent material. Other clays are also used for the manufacture of organoclay, depending on the application and location of mineral deposits.

Organoclay is commonly used in the upstream sector of the petroleum industry for removing hydrocarbons from refinery process water, but it has seen little use in petroleum production. Many other industries also use it, including shipping and dockside servicing, carwashes, and others dealing with an oily wastewater stream.

Organoclays have also been tested for treating ground and surface water for other organic chemicals such as PCBs and pesticides.

Present and Future Constraints on Oilfield Produced Water.

Oilfield produced water is an important source of surface water in the arid western U.S. The discharge of produced water is permitted under the National Pollutant Discharge Elimination System (NPDES), which may be administered by the U.S. E.P.A. or by a state program. In addition, other state and federal programs come into play to generally prohibit the presence of a free oil sheen or staining of the shoreline of surface impoundments.[1] Netting may also be required over surface impoundments in order to protect migratory birds from hydrocarbon contamination.[2] While livestock ranchers and state or federal agencies generally support produced water discharge, oil producers encounter difficulty when their discharges include free oil that results in a sheen or stain on the shoreline and contamination of wildlife and livestock.

In Wyoming, produced water discharges are regulated by the state Department of Environmental Quality. Generally, a produced water discharge into dry a ravine can be permitted if it contains less than 5,000 mg/l Total Dissolved Solids and less than 10 mg/l Oil and Grease. Other site-specific limits for Chemical Oxygen demand (COD), pH, Radium 226, or other parameters may exist, including Whole Effluent Toxicity (WET).[3] The DEQ protects existing water bodies with stricter limits. People who enjoy sport fishing in Wyoming will be glad to know that trout streams are well-protected.

The State of Wyoming currently holds 586 valid NPDES permits as of 1996 to discharge approximately 121,300 bbl. per day of produced water (1994)[4]. This amount represents approximately 31% of all produced water.

Several Federal initiatives may spell trouble for the future of produced water discharge. Most importantly, produced water discharge is possible only through an exemption in the Resource Conservation and Recovery Act (RCRA) - the hazardous waste regulations. Produced water usually contains sufficient benzene, toluene, ethylbenzene and xylene (BTEX compounds) that it would be classified as a hazardous waste if it were an industrial wastewater. Several reports by the EPA[5], American Petroleum Institute (API)[6], and the Interstate Oil and Gas Compact Commission (IOGCC)[7] have shown that the low toxicity of oilfield waste does not warrant full regulation by the EPA, but the future still remains in the hands of Congress. In the near term, the "E&P Exemption" is vital to the domestic oil and gas industry. The EPA Toxic Release Inventory (TRI) program enacted under the Superfund Amendments and Reauthorization Act (SARA) section 313 also appears to be a storm on the horizon, although the EPA recently removed E&P activities from inclusion in the program[8]. This reprieve may be only temporary, however.

For these and other reasons, the petroleum industry is pro-actively searching for new technology to economically remove free oil and soluble hydrocarbons from produced water.

Description of the ET Ventures - RMOTC Test

ET Ventures and RMOTC conducted a 24-hour test at the US Naval Petroleum Reserve #3 (Teapot Dome oil field) on July 11-12, 1996. The general intent of the test was to evaluate the ability of ET #1 to adsorb hydrocarbons from produced water. While the ability of ET #1 to adsorb hydrocarbons has been proven in the laboratory and in other applications, it was not known if the product would perform as expected in a field environment where waters carry a free oil sheen and where there are wide variations in hydrocarbon concentrations. It was also unknown whether it would perform well enough to reduce BTEX below RCRA contaminant levels. A 24-hour test was deemed long enough to accomplish the goals of the test.

Crude oil and associated water at NPR-3 are produced from the Tensleep formation, one of several Pennsylvanian - Permian formations that contribute most of the produced water that is discharged within Wyoming. Other formations that produce water capable of being discharged include the Minnelusa and the Phosphoria. NPDES discharge limits and chemical composition are presented in Tables 1 and 2.

One early complication of the field test was that the temperature of the water was higher than the maximum operating temperature of ET #1. Tensleep wells are pumped using high volume submersible electric pumps, bringing water and oil to the surface at nearly 200° F. Polymer loss from ET #1 becomes excessive above about 150°F, thus for testing purposes, Tensleep water was transferred from the usual holding tank to a portable storage tank two days before the test. This allowed the produced water to cool to approximately 95° F before the test began. The tank was agitated immediately prior to the test in order to disperse any crude oil that may have separated. ET Ventures test trailer consisted of the following equipment:

- An electric transfer pump rated for approximately 5 gallons per minute.
- A 0-10 GPM flow meter.
- Two 55-gallon drums containing ET Ventures Formula #1 (ET #1).
- One 55-gallon drum containing Granular Activated Carbon (GAC).
- Sample points for obtaining desired water samples.

A schematic diagram and photograph of the test equipment are shown as Figures 1 and 2. The drums were purchased from Tetrasolv, Inc. and include a spreader system and all the necessary inlet and outlet fittings. The equipment was installed so that water flowed upward from the bottom in drums containing ET #1, but downward through the GAC. This was done in order to avoid fluidizing the GAC and causing channeling through the media. The specific equipment used in the test operates at a maximum rate of 10 gpm, maximum temperature of 100°F, and at a maximum pressure of 10 psi.

Before the start of the test, the system was purged of air and filled one vessel at a time until the unit was completely filled with water. ET Ventures staff decided that there was no need for the system to reach dynamic equilibrium before sampling, so the transfer pump was started and the first sample was taken shortly thereafter.

Sampling

Samples were taken according to written procedures and EPA protocols to ensure the reliability of the analytical results. Procedures included the use of precleaned and sealed glassware, obtaining zero-headspace samples when necessary, chilling the samples to 4°C for storage and transportation, and delivery to a commercial lab within published holding times.

Four sets of samples (numbered 1-4) were obtained during the 24-hour test. Each set contained one upstream sample (sample A,), one sample taken between the second ET #1 container and the drum containing GAC (sample B), and one downstream sample (sample C). In this manner, one can compare contaminant concentrations across the process or look at a specific sample location over time.

Samples were analyzed for Oil & Grease (EPA Method 413.2), Total Petroleum Hydrocarbon (TPH - EPA method 418.1) and BTEX (EPA Method 8020). These analyses were believed to be the ones most interesting to industry due to their frequent use as regulatory parameters.

Test Results

The results of laboratory analyses are shown in Tables 4-8. After review of the test chronology and lab data, RMOTC and ET Ventures were able to conclude that the combination of ET #1 and granular activated carbon consistently and effectively removed hydrocarbons from produced water. Specific findings are that ET #1:

- Reduced Total Petroleum Hydrocarbons to non-detectable levels. In all four sets of samples, TPH was below detectable limits after adsorption by ET#1 alone (sample B).

- Reduced Oil and Grease to non-detectable levels. In three of four samples, Oil and Grease was below detectable limits after adsorption by ET #1 alone (sample B). The fourth sample detected Oil and Grease at the detection limit of 1.0 mg/l.

- Reduced soluble hydrocarbons: Benzene, Ethylbenzene, Toluene, and Xylene to barely detectable levels. In all four sets of samples, BTEX was barely detectable after adsorption by ET #1 alone (sample B). BTEX was below detectable limits after the combination of ET #1 and granular activated carbon (sample C).

In simple terms, ET #1 eliminated hydrocarbon contamination from produced water during the test. Other testing conducted by ET Ventures has shown that similar results are possible in large-scale commercial applications.[9]

Upstream Oil and Grease concentrations are higher during this test than normally encountered during NPDES sampling. The reasons for this are unknown, but it is possible that the frac tank or water truck used to haul the produced water contained additional oil beyond the amount contained in the produced water. Regardless, the test conditions represent a difficult case for treatment, having both high concentrations and wide variations in hydrocarbon content.

The End of the Line - Waste Disposal

Other laboratory testing of spent ET #1 has shown that BTEX and other volatile hydrocarbons are adsorbed tightly enough for the spent product to pass the EPA's Toxicity Characteristic Leachate Procedure(TCLP) test and be disposed as a non-hazardous waste. The TCLP is used to identify the presence or absence of toxic chemicals that might be able to leach into groundwater after disposal. This is an amazing accomplishment, given that the product may adsorb up to 88% of its own weight in hydrocarbons or 100% by volume.[9] This quality may also allow ET #1 to also be used as an adsorbent for controlling hydrocarbon fuel spills, although further discussion of that possibility is outside the scope of this report.

Being classified as a non-hazardous waste may allow the spent product to be landfilled, land farmed, or otherwise disposed in an economical manner. Available alternatives for non-hazardous waste disposal are always governed by local regulations, so a purchaser will have to investigate which options are actually available. In order to ensure that customers have at least one disposal option available, spent product can be returned to the manufacturer for the cost of freight. Another manufacturer of organoclays adds activated carbon directly to their product. This practice allows the spent material to be used as boiler fuel since its BTU content is high enough to meet regulatory requirements for energy recovery. Depending on the BTU content of the contaminant, spent ET #1 may contain up to 16,000 BTU/lb.[10]

Until enough experience is gained in disposing of the spent product, a prudent facility operator should verify these conclusions with their own TCLP testing prior to disposal. Not only is this required by RCRA, but there are other concerns that have not been addressed in this report. Chief among these concerns is whether ET #1 will concentrate heavy metals including radium 226 from produced water and whether it will bind them sufficiently to pass the TCLP criteria for metals.

Anticipated Operating Costs

Operating costs can be estimated from experience gained in other industries.[10] Capital expense necessarily depends on the required flow rate, but experience has shown that high pressure still bed filtration units may be amortized at approximately $0.001 per gallon of water treated. These units are nearly maintenance-free in their operation.

Product costs can be estimated using the following conservative assumptions:

- Inlet concentration of 100 ppm. oil & grease
- Oil specific gravity of 1.0
- Adsorbent loading factor of 72% (0.72 lb. oil/lb. ET #1)
- Purchase cost of ET #1 @ $3.00/lb

Lbs. oil per million gallons = ppm * S.G.*8.33#/gal. . . . . (1)

=100 ppm *(1.0 SG)*(8.33#/gal.)
= 833 lbs. oil per million gallons of wastewater

Using a loading rate of 0.72 pounds of oil adsorbed per pound of ET #1 results in a product requirement of 1,156 pounds ET #1 per million gallons at a total cost of $3,467. This translates into a product of cost of approximately $0.0035 per gallon treated. Addition of the $0.001 cited previously for amortization of the capital cost results in a total treatment cost of about $0.0045 per gallon of water treated. Disposal cost is not included.

Further Work

Further work with this product is being considered. A long-term test to determine loading capacity and breakthrough time under commercial conditions is being studied. Such a long-term test would also provide a better estimate of capital and operating expenses for a typical oilfield facility.

Acknowledgments

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References

1. *Discharge of Oil*, Title 40, U.S. Code of Federal Regulations, Part 110, 1996.

2. Migratory Bird Treaty Act, 6 USC Sections 701-715.

3. Wyoming Department of Environmental Quality, Water Quality Division:. *Regulations, Chapters 2 and 3*.

4. U.S. Department of Energy and Interstate Oil and Gas Compact Commission: *Oil and Gas Exploration and Production Waste Management - A 17 State Study*, Office of Scientific and Technical Information , Oak Ridge, TN (1993).

5. U.S. Environmental Protection Agency: *Report to congress: Management of Wastes Associated from Exploration, Development and Production of Crude Oil, Natural Gas, and Geothermal Energy*, NTIS Publication No. PB 88-146212, (1987).

6. American Petroleum Institute: *Onshore solid Waste Management in Exploration and Production Operations*, API Order No. 811-10850, (1989).

7. Interstate Oil and Gas Compact Commission (IOGCC): *EPA/ICC Study of State Regulation of Oil & Gas Exploration and Production Waste*, (1990).

8. Rubin, M. And Petten, K.: *Right-to-Know Reporting for the Oil and Gas Exploration and Production Industry*, paper SPE 37896 presented at the 1997 SPE/EPA Exploration & Production Environmental Conference, Dallas, March 3-5.

9. ET Ventures: internal communication.

10. ET Ventures: Personal communication.

Si metric Conversion Factors

Btu	x 1.055 056	E+00	= kj
ºF	(ºF-32)/1.8		= ºC
psi	x 6.894 757	E+00	= kPa
lbm	x 4.535 924	E-01	= kg
bbl	x 1.589 873	E-01	= m^3
gal	x 3.785 412	E-03	= m^3

Laboratory Data and Test Results

TABLE I - REPRESENTATIVE NPDES TEST RESULTS

	5-14-96	7-17-96	9-16-96
Oil & Grease	4.7 mg/l	6.2	4.2
COD	46 mg/l	108	37
Conductivity	7168 µmho/cm	6533	6140
pH	7.36	7.64	7.91
Radium 226	16.4 pci/l	-N/A-	-N/A-

TABLE 2 - MAJOR IONIC SPECIES PRESENT IN TENSLEEP WATER

CATIONS	mg/l	ANIONS	mg/l
Sodium	920.79	**Chloride**	1608.55
Calcium	290.00	**Bicarbonate**	96.00
Magnesium	46.17	**Sulfate**	547.56
Potassium	0.00	**Carbonate**	0.00

TABLE 3 - TOTAL PETROLEUM HYDROCARBON BY EPA METHOD 418.1

Location 1 (Upstream) Sample ID:	mg/l	Location 2 (After ET#1) Sample ID	mg/l	Location 3 (After GAC) Sample ID	mg/l
ETV#1A	148	ETV#1B	<1.0	ETV#1C	1.1
ETV#2A	20	ETV#2B	<1.0	ETV#2C	<1.0
ETV#3A	6.8	ETV#3B	<1.0	ETV#3C	1.3
ETV#4A	25	ETV#4B	<1.0	ETV#4C	<1.0

TABLE 4 - OIL & GREASE BY EPA METHOD 413.2

Location 1 (Upstream) Sample ID:	mg/l	Location 2 (After ET#1) Sample ID	mg/l	Location 3 (After GAC) Sample ID	mg/l
ETV#1A	151	ETV#1B	<1.0	ETV#1C	1.2
ETV#2A	18	ETV#2B	<1.0	ETV#2C	1.4
ETV#3A	7.4	ETV#3B	<1.0	ETV#3C	1.1
ETV#4A	79	ETV#4B	1.0	ETV#4C	<1.0

TABLE 5 - BENZENE BY EPA METHOD 8020

Location 1 (Upstream) Sample ID:	µg/l	Location 2 (After ET#1) Sample ID	µg/l	Location 3 (After GAC) Sample ID	µg/l
ETV#1A	3.14	ETV#1B	2.85	ETV#1C	<0.50
ETV#2A	1.81	ETV#2B	2.01	ETV#2C	<0.50
ETV#3A	0.90	ETV#3B	<0.50	ETV#3C	<0.50
ETV#4A	0.73	ETV#4B	<0.50	ETV#4C	<0.50

TABLE 6 -TOLUENE BY EPA METHOD 8020

Location 1 (Upstream) Sample ID:	µg/l	Location 2 (After ET#1) Sample ID	µg/l	Location 3 (After GAC) Sample ID	µg/l
ETV#1A	4.97	ETV#1B	<0.50	ETV#1C	<0.50
ETV#2A	2.03	ETV#2B	0.83	ETV#2C	<0.50
ETV#3A	0.86	ETV#3B	<0.50	ETV#3C	<0.50
ETV#4A	0.99	ETV#4B	<0.50	ETV#4C	<0.50

TABLE 7 - ETHYLBENZENE BY EPA METHOD 8020

Location 1 (Upstream) Sample ID:	µg/l	Location 2 (After ET#1) Sample ID	µg/l	Location 3 (After GAC) Sample ID	µg/l
ETV#1A	4.95	ETV#1B	<0.50	ETV#1C	<0.50
ETV#2A	0.90	ETV#2B	<0.50	ETV#2C	<0.50
ETV#3A	<0.50	ETV#3B	<0.50	ETV#3C	<0.50
ETV#4A	1.02	ETV#4B	<0.50	ETV#4C	<0.50

TABLE 8 - XYLENE(S) BY EPA METHOD 8020

Location 1 (Upstream) Sample ID:	µg/l	Location 2 (After ET#1) Sample ID	µg/l	Location 3 (After GAC) Sample ID	µg/l
ETV#1A	29.70	ETV#1B	<1.00	ETV#1C	<1.00
ETV#2A	11.9	ETV#2B	1.40	ETV#2C	<1.00
ETV#3A	3.61	ETV#3B	2.64	ETV#3C	<1.00
ETV#4A	5.95	ETV#4B	2.73	ETV#4C	<1.00

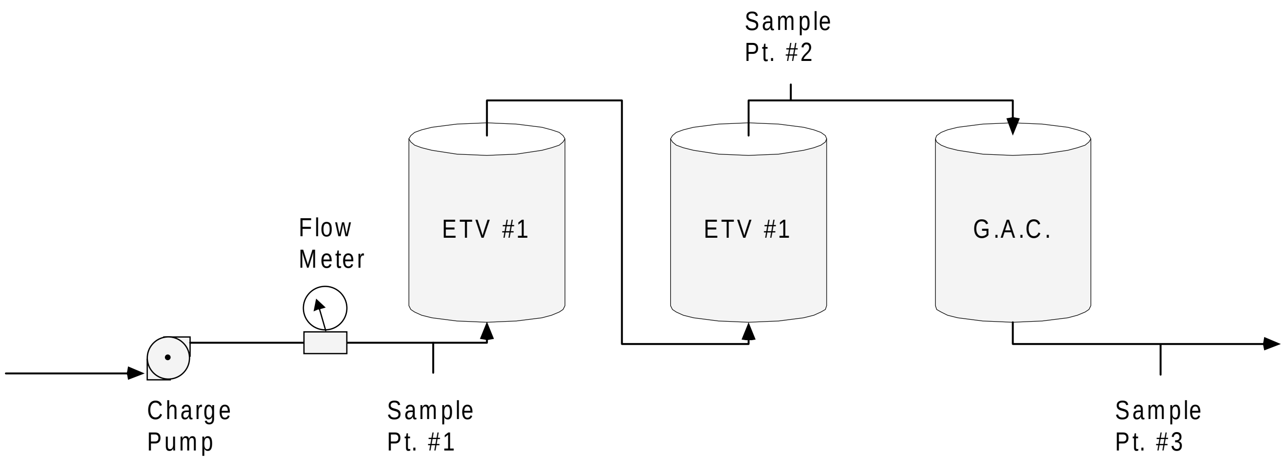

Fig.1 - Schematic of test equipment. Sample point #1 is the source of all "A" samples. "B" samples were taken from sample point #2, and "C" samples were drawn from point #3. Four sets of samples were taken during the 24-hour test period.

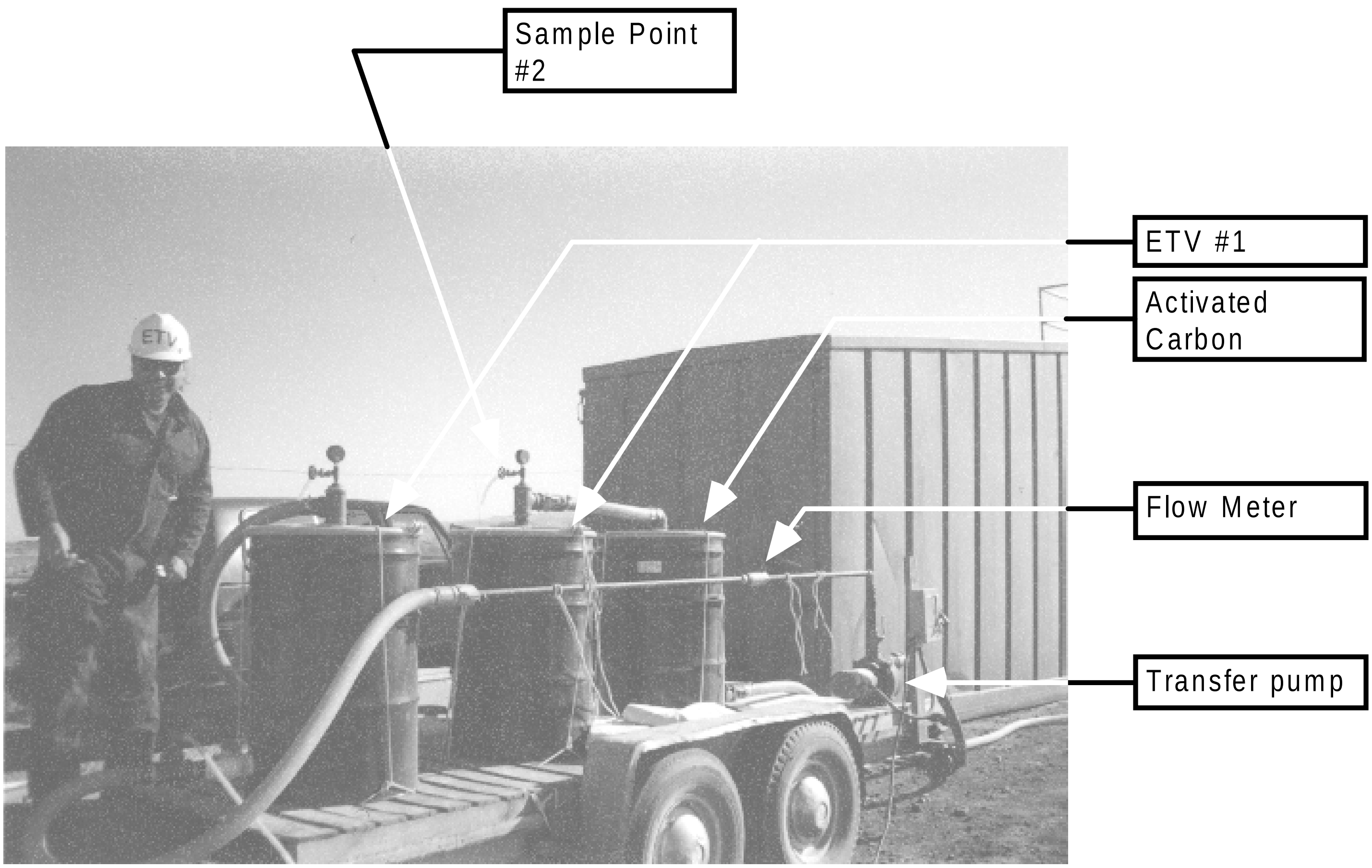

Fig.2 - Photograph of trailer-mounted equipment used for test. Water for test came from frac. tank in the background. Flow is from back-to-front in the foreground, and then front-to-back through the adsorbent canisters.